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Hydrogen Iodide/Zinc Iodide: A New Initiating System for Living Cationic Polymerization of Vinyl Ethers at Room Temperature[1]

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ABSTRACT: Zinc iodide in conjunction with hydrogen iodide (HI/ZnI_2) as an initiating system led to living cationic polymerization of isobutyl vinyl ether in toluene in a wide temperature range from −40 °C to above room temperature (+40 °C) or in methylene chloride below 0 °C. The HI/ZnI_2 system also induced living polymerization of an ester-functionalized vinyl ether (2-acetoxyethyl vinyl ether) in methylene chloride at −15 °C. In all cases, the number-average molecular weight of the polymers increased in direct proportion to monomer conversion and further increased on addition of a fresh feed of monomer at the end of the first-stage polymerization. The molecular weight distribution of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$) throughout the reaction. The polymer molecular weights at the same conversion were inversely proportional to the initial concentration of hydrogen iodide, whereas they were independent of the initial ZnI_2 concentration. The overall polymerization rate, however, progressively increased with increasing concentration of the zinc salt. It was proposed that ZnI_2, as a weak Lewis acid, electrophilically activates the hydrogen iodide derived CH–I terminal of the growing polymer and thereby induces living propagation, as iodine does in the living polymerization initiated by the hydrogen iodide/iodine system.

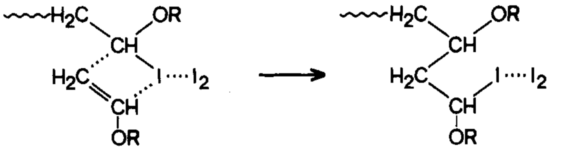
Introduction

A mixture of hydrogen iodide and iodine (HI/I_2) as an initiating system effectively polymerizes vinyl ethers[2] and related vinyl compounds to yield living polymers with a controlled molecular weight and a narrow molecular weight distribution (MWD).[3] Our spectroscopic[4] and kinetic[4,5] studies on the mechanism of these living processes demonstrated that hydrogen iodide generates the growing end, whereas iodine assists its living propagation. Specifically, hydrogen iodide, as an *electrophile*, quantitatively forms a 1:1 adduct [$CH_3CH(OR)$–I; R = alkyl, etc.] with a vinyl ether monomer at the initial stage of polymerization. Although the adduct per se is too stable to initiate vinyl ether polymerization, coexisting iodine electrophilically "activates" (dissociates or polarizes) its carbon–iodine (CH–I) bond and thereby allows the incoming monomer to add into the activated terminal linkage. Repetition of such an activation/addition process leads to living polymers bearing a CH–I terminal [~~~$CH_2CH(OR)$–I] that can in turn be activated by iodine to continue living propagation (eq 1).[5,6] Thus, iodine herein acts as a *Lewis acid* (electron acceptor).

A working hypothesis immediately drawn from this mechanism is that not only the HI/I_2 system but other appropriate combinations of an electrophile and a Lewis acid as well may serve to initiate living cationic polymerization of vinyl monomers. For these binary initiating systems, the electrophile should be such that it forms a stable yet potentially reactive propagating end corresponding to the terminal CH–I unit in the HI/I_2-initiated living polymer; the Lewis acid component should be suitably electrophilic so as to selectively activate the terminal group without inducing cationic polymerization by itself. We recently decided to pursue such binary initiating systems and to establish the scope of *electrophile/Lewis acid* combinations for living cationic polymerization.

In this first study of our series,[1] we selected zinc iodide (ZnI_2) as a Lewis acid to replace iodine in the HI/I_2 initiating system. Among zinc(II) halides, ZnI_2 has been employed least frequently as catalyst or initiator in Friedel–Crafts and related electrophilic reactions including cationic polymerization.[7] No report is thus far available for living cationic polymerization mediated by this iodide. More extensive use is found for zinc chloride and bromide;[7,8] quite recently they were utilized to initiate the group transfer (or "monomer cleavage") polymerization of trialkylsilyl vinyl ethers.[9]

Like iodine, ZnI_2 may interact electrophilically with the growing CH–I terminal, derived from hydrogen iodide, and may thus trigger living polymerization of vinyl ethers and other related monomers. Equations 1 and 2 visualize the expected similarity between the HI/I_2 and HI/ZnI_2 initiating systems. As described in this paper, we found the combination of hydrogen iodide and ZnI_2, as an electrophile/Lewis acid initiating system, to induce living cationic polymerizations of isobutyl vinyl ether (IBVE) and 2-acetoxyethyl vinyl ether (AcOVE; $CH_2{=}CHOCH_2CH_2OCOCH_3$). A particular advantage of the HI/ZnI_2 system over HI/I_2 is that it enables the synthesis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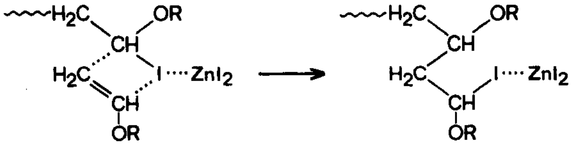
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of well-defined living polymers even *above room temperature.*

Experimental Section

Materials. Commercial IBVE was washed with 10% aqueous sodium hydroxide solution and then with water and dried overnight with potassium hydroxide pellets. AcOVE was prepared from 2-chloroethyl vinyl ether and sodium acetate as described.[10] Both monomers were distilled twice over calcium hydride (under reduced pressure for AcOVE) and sealed in ampules under dry nitrogen; gas chromatographic purity was >99.8%.

ZnI_2 (Aldrich, purity >99.99%) was used as received without further purification. It was quickly ground to a fine powder and dried under vacuum at room temperature in the dark for at least 24 h just before use. The subsequent handling of the light- and moisture-sensitive salt was done in the dark under dry nitrogen; no color due to liberated iodine was observed both in bulk and in solution. Anhydrous hydrogen iodide (as an *n*-hexane solution) and iodine were purified and used as previously reported.[2] Toluene, *n*-hexane, methylene chloride, and diethyl ether as solvents and carbon tetrachloride as an internal standard for gas chromatography were purified by the usual methods[2] and doubly distilled over calcium hydride just before use.

Procedures. Polymerizations were carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. The reactions were initiated by adding, via dry syringes, prechilled solutions of hydrogen iodide (in *n*-hexane; 0.50 mL) and ZnI_2 or iodine (in diethyl ether; 0.50 mL), sequentially in this order, into a monomer solution [in toluene or methylene chloride, 0.38 M (5.0 vol %); 4.0 mL] kept at the polymerization temperature. Thus, in all runs the polymerization solvent actually contained *n*-hexane and diethyl ether in 10 vol % each; for simplicity, however, it was designated as toluene or methylene chloride in the following text. After a predetermined interval, the polymerization was terminated with prechilled ammoniacal methanol. Conversion was determined from the residual monomer concentration measured by gas chromatography with carbon tetrachloride (2.5 vol %) as the internal standard.

The quenched reaction mixtures were washed with 10% aqueous sodium thiosulfate solution and then with water to remove the inorganic residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers. The MWD of the polymers was measured by size-exclusion chromatography in chloroform at room temperature on a Jasco Trirotar-II instrument equipped with three polystyrene gel columns (Shodex A-802, A-803, and A-804; *exclusion limit* 5×10^3, 7×10^4, *and* 5×10^5, respectively). The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from the size-exclusion chromatograms on the basis of a polystyrene calibration.

Results and Discussion

1. Polymerization of IBVE in Toluene.

The possibility of (living) cationic polymerization by the HI/ZnI_2 initiating system was first examined for IBVE, a simple alkyl vinyl ether, with the use of nonpolar toluene solvent. A wide temperature range from −40 to +40 °C was covered to establish the conditions of living polymerization, with particular attention focused on the difference and similarity between the HI/ZnI_2 and HI/I_2 initiators.

Living Polymerization above Room Temperature. We soon found that ZnI_2 in conjunction with hydrogen iodide effectively polymerizes IBVE in toluene at all temperatures employed. Figure 1 shows the time course of the polymerization at +25 °C (HI/ZnI_2 = 25:1 mole ratio), along with that for HI/I_2 otherwise under the same conditions. The HI/ZnI_2-initiated polymerization smoothly occurred without an induction phase and turned out to be much faster than the corresponding reaction by HI/I_2 initiator. The reaction mixtures with HI/ZnI_2 remained completely colorless and homogeneous throughout. Control experiments carried out in the absence of hydrogen iodide showed that ZnI_2 alone does not polymerize IBVE at all (the half-filled circle in Figure 1).

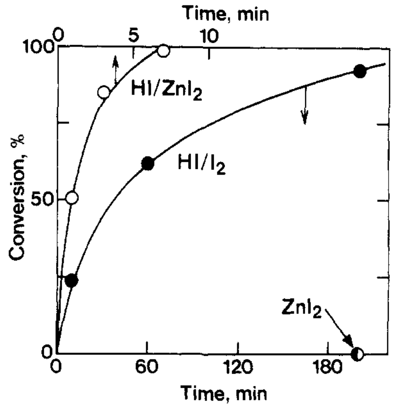

Figure 1. Time–conversion curves for the polymerization of IBVE in toluene at +25 °C: $[IBVE]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnI_2]_0$ = $[I_2]_0$ = 0.20 mM. Initiator: (○) HI/ZnI_2; (●) HI/I_2; (◐) ZnI_2.

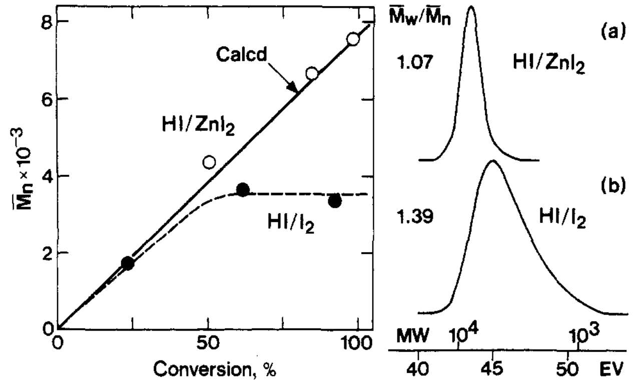

Figure 2. $\bar{M}_n$–conversion plots and MWD curves for poly(IBVE) obtained in toluene at +25 °C with HI/ZnI_2 and HI/I_2: $[IBVE]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnI_2]_0$ = $[I_2]_0$ = 0.20 mM. Conversions for MWD: (a) 98%; (b) 92%. The diagonal solid line in the $\bar{M}_n$–conversion profile indicates the calculated $\bar{M}_n$ values assuming one living polymer chain per unit hydrogen iodide.

The molecular weight ($\bar{M}_n$) of the polymers obtained with HI/ZnI_2 in the experiment for Figure 1 increased in direct proportion to monomer conversion (Figure 2). The $\bar{M}_n$ values, though based on a polystyrene calibration, were in excellent agreement with the calculated values assuming that one polymer chain forms per unit hydrogen iodide (the solid line in Figure 2). The MWD of the polymers was quite narrow and close to a monodisperse distribution, maintaining the $\bar{M}_w/\bar{M}_n$ ratio below 1.1 over the whole conversion range (e.g., curve a, Figure 2). In sharp contrast, the corresponding polymers formed by HI/I_2 has a broader MWD ($\bar{M}_w/\bar{M}_n$ = 1.3–1.4; e.g., curve b, Figure 2), the $\bar{M}_n$ of which soon leveled off after an initial rise at the early stage of the polymerization. These facts show that the HI/ZnI_2 system leads to well-defined living polymerization of IBVE in toluene even at room temperature, whereas the HI/I_2 system does not.

The living nature of the HI/ZnI_2-initiated polymerization was further demonstrated by so-called "monomer-addition" experiments where a fresh feed of IBVE was added to the reaction mixture just before or immediately after the initial charge of the monomer had been completely polymerized (i.e., at conversion 95–100%) (Figure 3). The added IBVE feed (equivalent to the first charge) was smoothly polymerized at nearly the same rate as in the first stage. The polymer molecular weight further increased in direct proportion to monomer conversion and was close to the calculated value for living polymers. The MWD of the polymers stayed narrow ($\bar{M}_w/\bar{M}_n$ = 1.1–1.2) even after the monomer addition, though somewhat

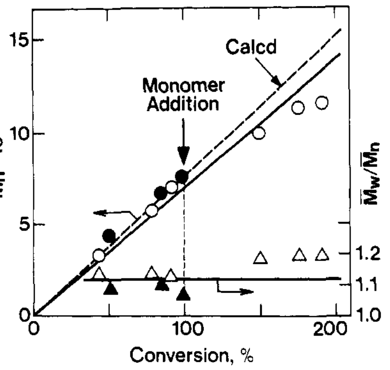

Figure 3. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(IBVE) obtained in a monomer-addition experiment in the polymerization by HI/ZnI$_2$ in toluene at +25 °C: $[IBVE]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnI_2]_0$ = 0.20 mM. The molar amount of the second IBVE feed was the same as in the first. The diagonal broken line indicates the calculated $\bar{M}_n$ values assuming one living polymer chain per unit hydrogen iodide. The different symbols designate replicated experiments.

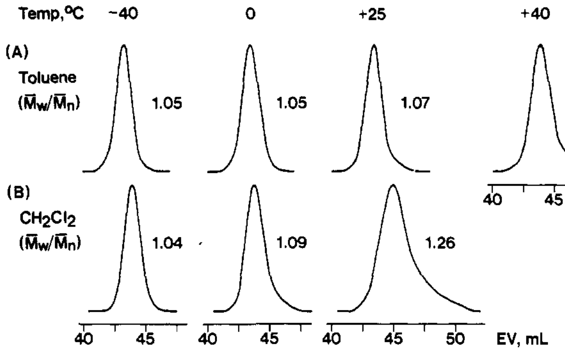

Figure 4. Effects of polymerization temperature on the MWD of poly(IBVE) obtained with HI/ZnI$_2$ in (A) toluene and (B) methylene chloride: $[IBVE]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnI_2]_0$ = 0.20 mM; conversion > 85%.

broader than those for the first-stage polymerization.

Effect of Polymerization Temperature. Experiments similar to the above were extended to a temperature range from −40 to +40 °C. At each temperature, the HI/ZnI$_2$ system effectively polymerized IBVE to quantitative conversion to give living polymers whose $\bar{M}_n$ increased proportionally to monomer conversion. As shown in Figure 4A, the polymers exhibited very narrow MWDs; the $\bar{M}_w/\bar{M}_n$ ratio stayed well below 1.1 for temperatures lower than +25 °C and less than 1.2 even for +40 °C. Thus, the HI/ZnI$_2$ system induces living polymerization of IBVE in toluene not only at low temperatures but *above room temperature* (+25 and +40 °C) as well.

2. Polymerization of IBVE in Methylene Chloride: Effects of Solvent Polarity. Polymerization of IBVE by HI/ZnI$_2$ was also carried out in methylene chloride as a relatively polar solvent at temperatures ranging from −40 to +25 °C. In all cases, the binary initiating system (HI/ZnI$_2$ = 25:1 mole ratio) polymerized IBVE to quantitative conversion; no polymers were formed in the presence of the zinc salt alone. As usual in cationic polymerization, the reactions were faster in a more polar solvent or at a higher temperature. The following data on the time (in min) for 100% conversion show such trends ($[IBVE]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnI_2]_0$ = 0.20 mM):

	temp, °C				
solv	−40	−15	0	+25	+40
toluene	>200		60	7	4
CH$_2$Cl$_2$	160	30	14	4	

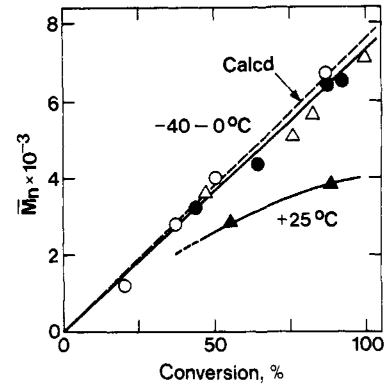

Figure 5. $\bar{M}_n$-conversion plots for poly(IBVE) obtained with HI/ZnI$_2$ in methylene chloride at −40 to +25 °C: $[IBVE]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnI_2]_0$ = 0.20 mM. Polymerization temperature (°C): (○) −40; (△) −15; (●) 0; (▲) +25. The diagonal broken line indicates the calculated $\bar{M}_n$ values assuming one living polymer chain per unit hydrogen iodide.

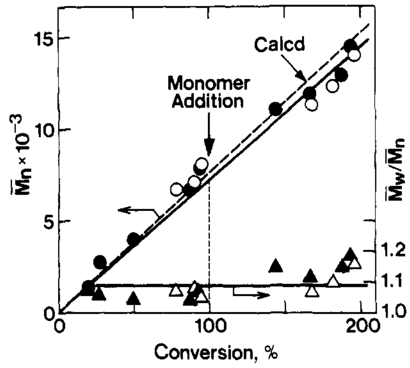

Figure 6. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(IBVE) obtained in a monomer-addition experiment in the polymerization by HI/ZnI$_2$ in methylene chloride at −40 °C: $[IBVE]_0$ = 0.38 M; $[HI]_0$ = 5.0 mM; $[ZnI_2]_0$ = 0.20 mM. The molar amount of the second IBVE feed was the same as in the first. The diagonal broken line indicates the calculated $\bar{M}_n$ values assuming one living polymer chain per unit hydrogen iodide. The different symbols designate replicated experiments.

Figure 5 plots the $\bar{M}_n$ values of the polymers, obtained in methylene chloride at four temperatures, as a function of monomer conversion. Their MWDs were compared in Figure 4B. In the polymerizations carried out below 0 °C, the polymer molecular weights were directly proportional to conversion and in excellent agreement with the calculated values for living polymers (one polymer chain per unit hydrogen iodide). The polymers had a very narrow MWD with $\bar{M}_w/\bar{M}_n$ < 1.1 as seen Figure 4B. At a higher temperature (+25 °C), however, the MWD became broader, and the $\bar{M}_n$ was clearly smaller than those for the lower temperatures, though it increased slightly as the polymerization proceeded (filled triangles, Figure 5).

Similarly, the HI/I$_2$ initiator led to living polymerization of IBVE at temperatures from −40 to 0 °C.[11]

"Monomer addition" experiments were carried out in the HI/ZnI$_2$-initiated polymerization in methylene chloride at −40 °C (Figure 6). The added IBVE was smoothly polymerized to give polymers whose $\bar{M}_n$ maintained the linear progressive increase with conversion commenced in the first-stage polymerization. The MWD of the polymers remained very narrow ($\bar{M}_w/\bar{M}_n$ < 1.2) before and after the monomer addition. Thus, the HI/ZnI$_2$ system (as well as HI/I$_2$) was found to initiate living polymerization of IBVE in not only toluene but also polar methylene chloride solvents; for the latter, however, the polymerization temperature should be below 0 °C.

3. Kinetics of the Living Polymerization by HI/ZnI$_2$ Initiator. The above-described results show that

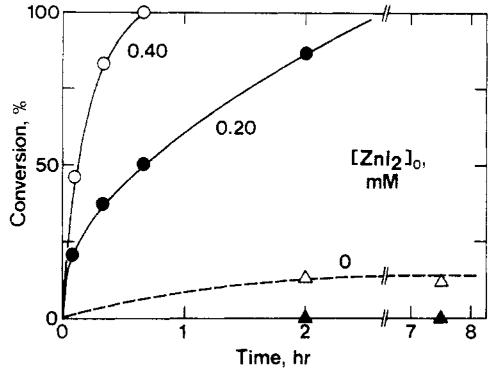

Figure 7. Effects of the initial ZnI_2 concentration on the IBVE polymerization by HI/ZnI_2 in methylene chloride at −40 °C: $[IBVE] = 0.38$ M; $[HI]_0 = 5.0$ mM. $[ZnI_2]_0$ (mM): (○) 0.40; (●) 0.20; (△) none; (▲) 0.20 (without hydrogen iodide).

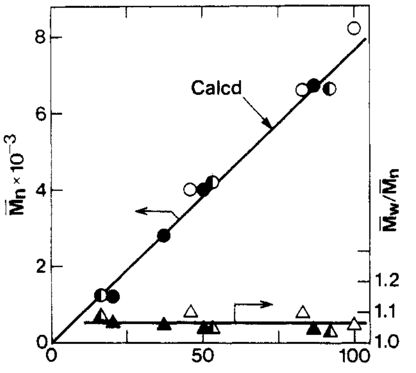

Figure 8. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(IBVE), obtained with HI/ZnI_2 and HI/I_2 in methylene chloride at −40 °C, as a function of monomer conversion: $[IBVE]_0 = 0.38$ M; $[HI]_0 = 5.0$ mM. $[ZnI_2]_0$ (mM): (○,△) 0.40; (●,▲) 0.20. (◐,▲) With HI/I_2; $[HI]_0 = 5.0$ mM, $[I_2]_0 = 0.20$ mM. The diagonal solid line indicates the calculated $\bar{M}_n$ values assuming one living polymer chain per unit hydrogen iodide.

the combination of ZnI_2 with hydrogen iodide, similar to the HI/I_2 pair, is an efficient initiating system for living cationic polymerization of IBVE. This section discusses experiments directed toward uncovering the roles of ZnI_2 and hydrogen iodide in these living processes.

Effect of ZnI_2 Concentration. A series of polymerizations were carried out in methylene chloride at −40 °C in which the initial concentration of ZnI_2 was varied, while that of hydrogen iodide was kept constant (Figure 7). As mentioned before, ZnI_2 alone (in the absence of hydrogen iodide) could not polymerize IBVE both in toluene (Figure 1) and in methylene chloride (filled triangles, Figure 7).

In the absence of the zinc salt, a sluggish polymerization was induced by hydrogen iodide alone to give a ca. 50% conversion in 20 h. The coexistence of a minute amount of ZnI_2 (less than 10 mol % relative to the hydrogen iodide) remarkably accelerated the polymerization where the overall rate increased with increasing ZnI_2 concentration.

Despite such rate differences, all these polymerizations at different HI/ZnI_2 mole ratios were living. The $\bar{M}_n$ of the polymers was directly proportional to monomer conversion and close to the calculated values for living polymers based on the IBVE/HI feed ratio (Figure 8). The MWD was very narrow with $\bar{M}_w/\bar{M}_n$ well below 1.1. More important, the $\bar{M}_n$–conversion plots for different ZnI_2 concentrations fell on a single straight line passing through the origin, indicating that the polymer molecular weight is independent of the initial ZnI_2 concentration.

Effect of Hydrogen Iodide Concentration. In another series of experiments, IBVE was polymerized by HI/ZnI_2 at varying concentrations of hydrogen iodide while that of ZnI_2 was set constant. As shown in Figure 9, the polymer molecular weights obtained at 100% conversion were directly proportional to the feed ratio ($[IBVE]_0/[HI]_0$) of IBVE to hydrogen iodide, or its was inversely proportional to the initial concentration of the protonic acid. The observed $\bar{M}_n$ values were in good agreement with those calculated with the assumption that one hydrogen iodide molecule forms one living polymer chain. The MWD of the polymers stayed very narrow over the whole range of the $[IBVE]_0/[HI]_0$ ratio up to 400.

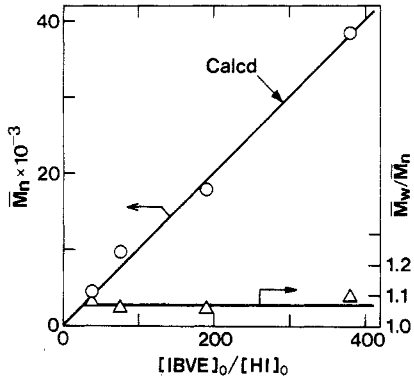

Figure 9. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(IBVE), obtained with HI/ZnI_2 in methylene chloride at −40 °C, as a function of the feed ratio of IBVE to hydrogen iodide: $[IBVE]_0 = 0.38$ M; $[ZnI_2]_0 = 0.20$ mM; $[HI]_0 = 1.0$–10 mM; conversion = 100%. The diagonal solid line indicates the calculated $\bar{M}_n$ values assuming one living chain per unit hydrogen iodide.

Table I
Living Polymerization of IBVE by HI/ZnI_2 and HI/I_2. Effects of Reaction Conditions[a]

solv	toluene				CH_2Cl_2			
temp, °C	−40	0	+25	+40	−40	−15	0	+25
HI/ZnI_2	yes	yes	yes	yes	yes	yes	yes	no
HI/I_2	yes	yes	no	no	yes	yes	yes	no

[a] $[IBVE]_0 = 0.38$ M (5.0 vol %); $[HI]_0 = 5.0$ mM; $[ZnI_2]_0 = [HI]_0 = 0.20$ mM.

These kinetic studies demonstrate that in the HI/ZnI_2-initiated living polymerization, hydrogen iodide is solely responsible for the generation of the propagating species, whereas ZnI_2 accelerates the living process. The same conclusion was reached for the living polymerization of vinyl ethers initiated by HI/I_2.[4,11] Therefore, the living propagation step with the HI/ZnI_2 system can be schematically expressed as eq 2 (see Introduction) which parallels eq 1 for the HI/I_2 system.

In accordance with this mechanistic similarity, the $\bar{M}_n$–conversion profiles for the living polymers produced by both HI/ZnI_2 and HI/I_2 initiators completely overlapped with each other, provided that the initial concentration of hydrogen iodide was the same (see Figure 8; filled circles for HI/ZnI_2 and half-filled circles for HI/I_2).

4. Living Polymerization of a Vinyl Ether (AcOVE) with an Ester Pendant. The HI/ZnI_2 initiating system was also applicable to AcOVE, an ester-containing vinyl ether that undergoes living polymerization in the presence of HI/I_2.[10] The acetoxy monomer was cleanly polymerized by HI/ZnI_2 in methylene chloride solvent at −40 °C to quantitative conversion. The resultant polymers exhibited a very narrow MWD ($\bar{M}_w/\bar{M}_n < 1.1$), and their $\bar{M}_n$'s increased proportionally to monomer conversion (Figure 10). Thus, the HI/ZnI_2 system produces living polymers from the functionalized vinyl ether with an ester pendant as well as from the nonpolar alkyl derivatve (IBVE). Details of the living AcOVE polymerization

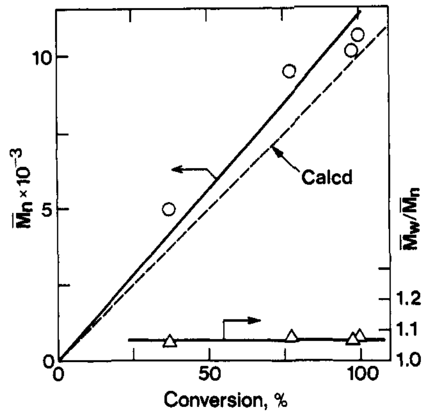

Figure 10. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(AcOVE), obtained with HI/ZnI$_2$ in methylene chloride at −15 °C, as a function of monomer conversion: $[\mathrm{AcOVE}]_0 = 0.38$ M; $[\mathrm{HI}]_0 = 5.0$ mM; $[\mathrm{ZnI_2}]_0 = 2.0$ mM. The polymerization was completed in 4.5 h. The diagonal broken line indicates the calculated $\bar{M}_n$ values assuming one living polymer chain per unit hydrogen iodide.

by HI/ZnI$_2$ will be reported elsewhere.

5. Reaction Conditions for Living Polymerization: HI/ZnI$_2$ vs. HI/I$_2$. Table I summarizes the overall results obtained in this study, where the range of reaction conditions for living polymerization of IBVE is shown as a function of polymerization solvent, temperature, and initiating systems. Inspection of Table I reveals the superiority of HI/ZnI$_2$ to HI/I$_2$; namely, only the former allows living polymerization of IBVE to occur in toluene solvent even above room temperature. The maximum temperature for living polymerization is as high as +40 °C (or above) with HI/ZnI$_2$ but just below 0 °C with HI/I$_2$. Another advantage of the ZnI$_2$-based system is the higher polymerization rate (cf. Figure 1) that permits an efficient polymer synthesis based on the living process.

An important difference between the two initiating systems is that ZnI$_2$ alone cannot polymerize IBVE, whereas iodine can even in the absence of hydrogen iodide. The contribution of the initiation by iodine itself may increase at a higher temperature, and the resulting parallel initiation by HI/I$_2$ and iodine may render the control of the $\bar{M}_n$ and MWD of polymers difficult in the HI/I$_2$-initiated polymerization above 0 °C where it fails to give living polymers.

Table I also shows the living polymerization by HI/ZnI$_2$ above room temperature (>+25 °C) to be feasible only in nonpolar toluene solvent. The temperature must be lowered to 0 °C or below to achieve living processes in more polar methylene chloride where the propagating end (CH–I terminal) is more dissociated or polarized and hence less stable.[3a]

The achievement of living cationic polymerization by the HI/ZnI$_2$ system provides positive evidence for our mechanism (eq 1 and 2)[4] that involves electrophilic activation of a CH–I terminal bond by a Lewis acid such as ZnI$_2$ and iodine. An extensive search of new initiating systems for living cationic polymerization based on our principle of the electrophile/Lewis acid combinations is now under way.

Registry No. IBVE (homopolymer), 9003-44-5; IBVE, 109-53-5; AcOVE (homopolymer), 31742-55-9; AcOVE, 6026-79-5; HI, 10034-85-2; ZnI$_2$, 10139-47-6.

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